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A systematic study on effect of electron beam irradiation on electrical properties and thermopower of $RE_{0.8}Sr_{0.2}CoO_3$ (RE = La, Pr) cobaltites

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ABSTRACT

The effect of electron beam (e-beam) irradiation on the crystal structure and transport properties of polycrystalline samples of $La_{0.8}Sr_{0.2}CoO_3$ (LSCO) and $Pr_{0.8}Sr_{0.2}CoO_3$ (PSCO) cobaltites is reported in this communication. The of X-ray diffraction data reveals that the pristine and irradiated compounds of LSCO and PSCO samples are single phased having rhombohedral structure with *R*-3C space group. It is noticed that the crystal structure is preserved even after irradiation. Nonetheless the unit cell parameters are slightly altered when exposed to e-beam. The resistivity patterns of LSCO and PSCO samples demonstrate the occurrence of semiconducting behavior over the measured temperature range of 10–300 K. From the analysis of the temperature dependent resistivity data on the bulk samples, it is seen that small polaron hopping (SPH) mechanism is more dominating in the high temperature region of the pristine sample as compared to e-beam irradiated samples of LSCO and PSCO. The Seebeck coefficient (*S*) data of all the batches of LSCO and PSCO samples predominantly display positive values over a vast temperature region, indicating that holes are the dominant charge carriers. The investigation of *S* measurements confirms the validity of *SPH* mechanism in the high temperature region.

1. Introduction

Rare earth based perovskite cobaltites with the formula $RECoO_3$ (where RE is a rare earth element like La, Pr) attracted much attention not only due to its complexity but also due to their fascinating temperature dependent nature of electronic and magnetic properties [1–6]. Even though cobaltites with mixed valence have been studied vastly, there is still room for thorough and systematic understanding of these rare earth perovskites. Since the perovskite based cobalt oxides are highly correlated systems, it provides a variety of phases such as metallic and semiconducting phases with different types of charge ordering, orbital ordering, magnetic ordering, and structural disorientations [7–10]. In addition to this, cobaltite families are also interesting because of their various applications. $La_{1-x}Sr_xCoO_3$ cobaltites are widely used as CO (carbon monoxide) sensors for efficient combustion control and are also well known for their use as effective material for cathode in solid oxide fuel cells (SOFC) [11], whereas $Pr_{1-x}Sr_xCoO_3$ system is a prototypical system in which one can explore the behavior of the material when substituting La^{3+} with Pr^{3+}. The bulk sample of paramagnetic $Pr_{1-x}Sr_xCoO_3$ has slightly smaller lattice parameters and a distorted perovskite like structure compared to rhombohedrally distorted bulk $La_{1-x}Sr_xCoO_3$ cobaltites, which is due to the smaller ionic size of Pr^{3+} [11,12].

Another interesting property of cobaltite is that the La^{3+} or Pr^{3+} can create chemical pressure in the system thus affecting Co—O—Co bond angles, this in turn results in narrower bandwidth e_g and a larger spin gap, because of this the stability of the low spin (*LS*) state in $RECoO_3$ compound improves. This results in a transition which in turn is the beginning of the spin state transition from about 30 K to ≥200 K which is observed especially in $PrCoO_3$ system [11]. Interestingly one can modify the transport properties of $RECoO_3$ using doping technique which is carried out by means of creating holes, in this case Co^{4+}. This phenomenon could be accomplished either by the oxidative non-stoichiometry as seen in $RECoO_{3+\delta}$ or by simply substituting divalent cations like Sr, Ca and Bi. (e.g. $La_{1-x}Sr_xCoO_3$ and $Pr_{1-x}Sr_xCoO_3$). Apart from these techniques, one can tailor several physical characteristics and properties merely by applying certain degree of external perturbations like magnetic field, pressure and irradiation [13–17]. One of the widely used methods is thermal annealing, but unfortunately it is observed that the size of the grains increases during this process and this

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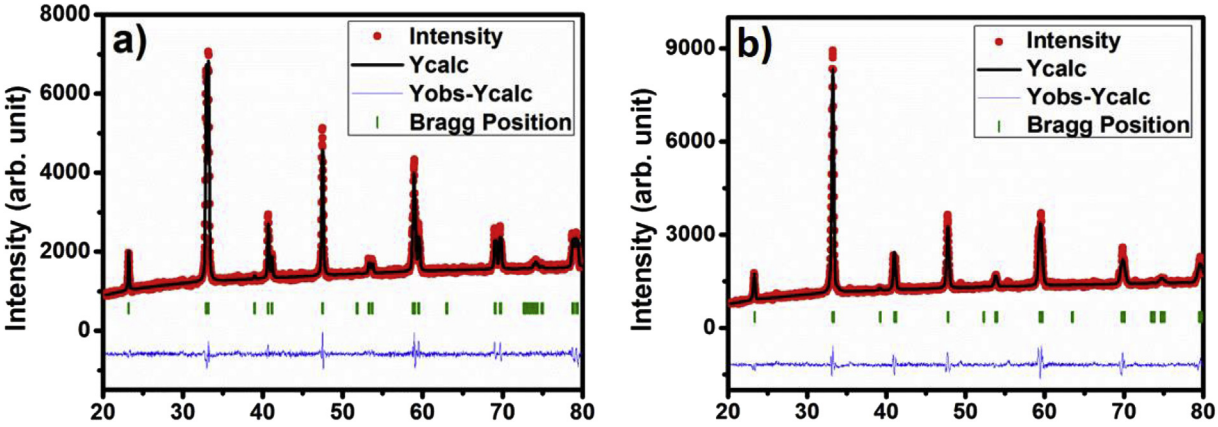

Fig. 1. Rietveld refinement plots of (a) pristine LSCO sample and (b) pristine PSCO sample.

conveys that there is less control over the size of the grains in the crystal. In order to have better control over tailoring various properties, highly energetic particle irradiation is used. Irradiation of electrons, neutrons, and ions were recognized to be one of the effective methods which are good alternatives to thermal annealing [17–20]. Irradiation of matter using particles with very high energy such as electrons and ions usually gives rise to formation of atomic defects in the target and hence affects the material properties [17,21–24]. In fact, the ABO_3 perovskite compound has a three dimensional network formed by BO_6 octahedron. The octahedra are essentially contently bonded. In the space created by these octahedral, sits the A-ion forming another sub lattice mainly governed by Coulombic interaction. Thus the distortion created by various substitutional ions creates distortions such as octahedral tilts, positional shift in B-ion and A-ion transnational motion against octahedra resulting into modification in electronic band structure. Defects are also responsible for such distortions, however, electrical conduction depends on hopping of different kinds as well as polaron hopping, etc that provides basis for understanding the transport properties in these materials. Irradiation using electron beam and ion beams have usually been used for tailoring the material properties of semiconductors, CMR materials, thermoelectric materials and nanostructured compounds [17,25–28]. To the best of our knowledge, there are no reports on effect of electron beam irradiation on electrical properties and thermopower of La and Pr-based coboltites. Keeping this in mind, we have investigated the effect of electron beam irradiation on electrical and thermoelectric properties of $RE_{0.8}Sr_{0.2}CoO_3$ (RE = La, Pr) systems.

2. Experimental procedure

Polycrystalline coboltite samples of $La_{0.8}Sr_{0.2}CoO_3$ (LSCO) and $Pr_{0.8}Sr_{0.2}CoO_3$ (PSCO) cobaltites were synthesized by means of conventional solid state synthesis method. Stoichiometric amounts of analytical grade La_2O_3, Pr_6O_{11}, $SrCO_3$ and Co_3O_4 powders with the purity of 99.9% (Sigma-Aldrich) were used for synthesis of the samples. Each precursor is first heated for 8 h at 750 °C separately before it is mixed and ground into fine stoichiometric mixture. The mixture is then calcined for 1100 °C several times for about 20 h with intermediate grindings. After calcination, the powder mixture was made into thin rectangular pellets of thickness ≈1.4 mm using hydraulic press. The pellets were sintered at a temperature of 1350 °C for 30 h and then cooled naturally inside the furnace to ambient temperature. Same batches of the samples were then exposed to irradiation of high energy electron beam (e-beam) using a particle accelerator. The irradiation process was carried out at ambient temperature condition and the beam energy of the incident electrons was 7.5 MeV. The irradiation process was performed at various dosages of 50 kGy, 100 kGy and 200 kGy. One pellet was kept unirradiated from the same batch so as to study the effect of e-beam irradiation on structural, electrical and thermo-electric properties. Room temperature powder *X-ray Diffraction* technique was used to study the crystal structure of crystalline samples of LSCO and PSCO using *Mini Flex II DESK TOP X-ray Diffractometer* which uses Cu-Kα as source (wavelength, λ = 1.54059 Å). The temperature dependent resistivity of the thin rectangular pellets was measured using a standard four probe experiment and was performed in a closed cycle refrigerator in the temperature range 10–300 K. The thermo-electric power (TEP) was also measured in the temperature range 10–300 K using differential dc method.

3. Results and discussion

3.1. Structural properties

Room temperature X-ray diffraction data was recorded for the pristine and e-beam irradiated samples of $La_{0.8}Sr_{0.2}CoO_3$ and $Pr_{0.8}Sr_{0.2}CoO_3$. The experimentally obtained XRD plots along with the theoretically simulated Rietveld refined plots for typical samples are shown in Fig. 1. In Fig. 1, the red open circles show the recorded experimental curve and the simulated plot is superimposed on them as a black curve, the vertical lines symbolize the Bragg's peak and the curve at the bottom shows the difference between the experimentally recorded and the theoretically simulated pattern. From the plots the reliable agreement between the calculated and the observed data is obtained and it confirms that the synthesized samples do not show any secondary or impurity phases. Further it is confirmed from Rietveld analysis that they have rhombohedral structure with space group *R*-3C. The same was observed for all the samples. The information on structural parameters obtained from refinement is listed in Table 1 along with the reliability factor (R_f).

For the LSCO samples, the cell parameters *a* (*b* or *c*) almost remains unaltered for e-beam dosage upto 100 kGy. However cell parameter is noticed to decrease when the e-beam dosage is raised to 200 kGy. We can also notice that unit cell volume remains unchanged for dosage of e-beam irradiation upto 100 kGy and then decreases for the sample irradiated with 200 kGy. In the case of PSCO, the lattice parameter *a* (or *b*) initially decreases for e-beam dosage of 50 kGy. Thereafter it is observed to increase with e-beam dosage of 100 kGy and with further increasing the dosage of e-beam, the parameter *a* remains unaltered. The lattice parameter *c*, however, is found to drop with increase in dosage of e-beam irradiation. One can observe from Table 1 that unit cell volume drops drastically with 50 kGy dosage of electron beam irradiation and then increases for higher dosage of 100 and 200 kGy.

We will now consider the effect of e-beam irradiation on the bond length. Usually when one irradiates the sample with highly energetic particles, there will be two significant effects of irradiation on crystalline solids viz., creation of vacancies or point defects due to